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AMERICAN DYESTUFF REPORTER

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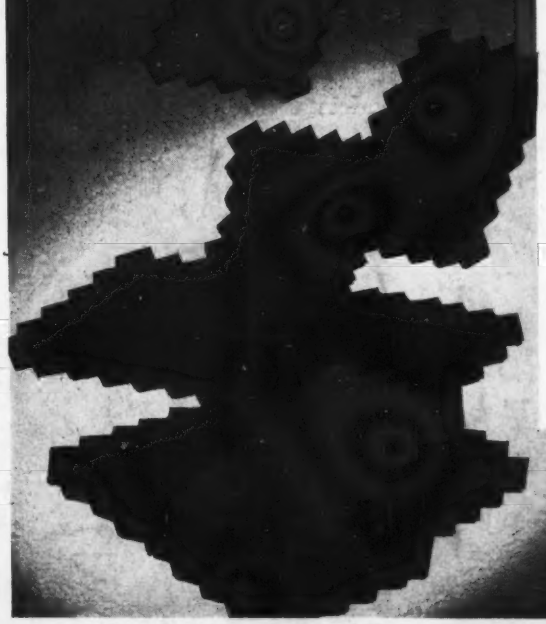

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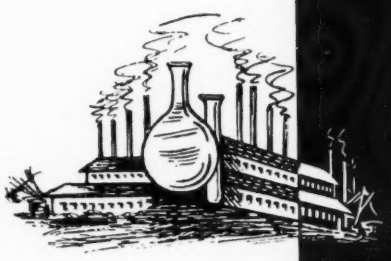

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THE ROLE OF CYSTINE

in the Structure of the Fibrous Protein, Wool

W. I. PATTERSON, W. B. GEIGER, L. R. MIZELL and M. HARRIS

Abstract

Wool is remarkable among textile materials in that it possesses high extensibility and the ability to return to its original length or shape after being stretched or distorted. These properties are of advantage in such products as clothing, blankets, and carpets. It is shown that a number of the important physical properties as well as some of the chemical properties of wool are dependent upon a unique molecular structure, provided by the presence of disulfide or cystine cross-linkages between the main molecular chains of the fiber. As a result, wool fibers possess a three-dimensional molecular network while most other textile fibers are composed of bundles of chain-like molecules, arranged more or less parallel to the axes of the fibers.

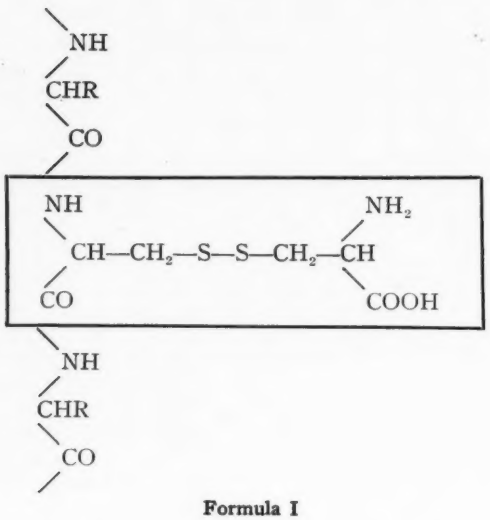
The role of these disulfide cross-linkages is made clear by a study of the behavior of wool before and after alteration of the mode of linkage of the sulfur. For example, the disulfide cross-linkages are readily broken to form sulfhydryl groups by the reducing agent, thioglycolic acid. The sulfhydryl groups of the reduced fibers readily react with alkyl halides to form thioether groups with two possible results. Thus, the reaction of reduced wool with alkyl monohalides results in permanent rupture of disulfide linkages and greatly increases the extensibility and decreases the strength of the fibers. The reaction with aliphatic dihalides introduces hydrocarbon chains between pairs of sulfur atoms of cystine molecules in the fibers. Such fibers are very similar to untreated fibers in physical properties.

Wools in which the disulfide linkages have been broken by reduction, or by reduction followed by treatment with alkyl monohalides possess much higher alkali-solubilities than untreated wool, while wools in which the disulfide cross-linkages have been replaced by new cross-linkages through reduction followed by reaction with dihalides possess much lower alkali-solubilities. Since the susceptibility of wool to degradation by alkalies is one of its greatest disadvantages, practical processes that would make it stable at its cross-linkages should also enhance its durability.

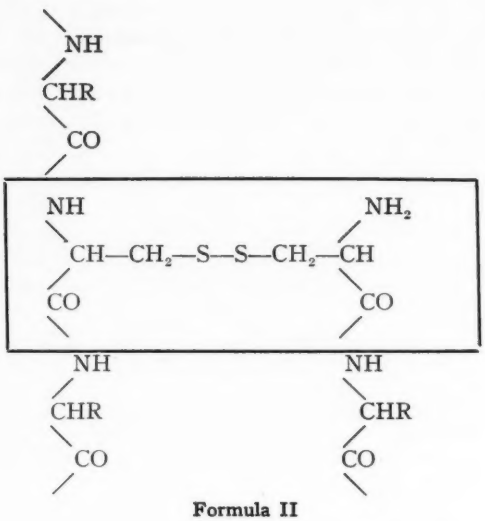
I. INTRODUCTION

PROTEINS, according to the hypothesis of Hofmeister[1] and Fischer[2], consist of amino acids joined through amide (peptide) linkages to form long chain structures called polypeptides. On the basis of this hypothesis, many of the similarities among proteins should be due to the large number of peptide linkages, while dissimilarities among them should be related to variations in the proportions and arrangement of the constituent amino acids, to differences in the lengths and arrangement of the polypeptide chains, and to the presence of linkages other than peptide. The present paper is concerned with the relationship of one such linkage, the disulfide linkage of the amino acid cystine, to the properties of the fibrous protein, wool.

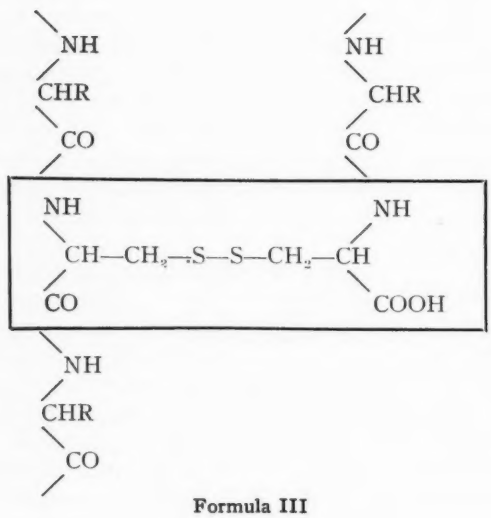
Although cystine contains two amino and two carboxyl groups, it appears that all of these groups are involved in peptide links in most, if not all, of the cystine residues. If the cystine of wool were combined in a peptide chain only through amino and carboxyl groups attached to the same carbon atom (Formula I), processes that break disulfide bonds should result in the elimination from the wool of one-half of the sulfur. This possibility is not supported by experiment, since reduced wool contains as much sulfur as the original material. Were either (or both) of the amino groups of cystine uncombined (Formula II), treatment of wool with nitrous acid would destroy at least half of the cystine in the former case and all of it in the latter. The investigations of Hess and Sullivan[3], as well as unpublished work in this laboratory,



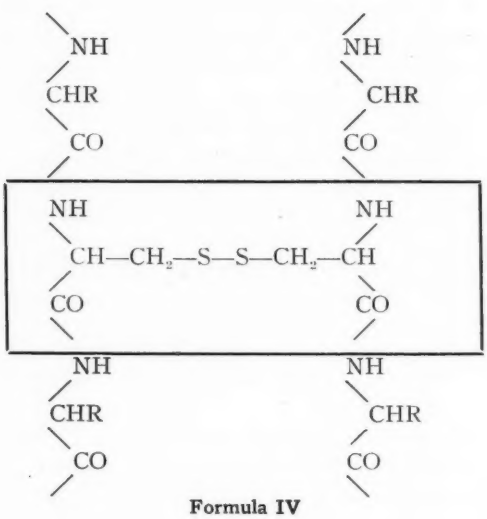
Formula I



Formula II



Formula III



Formula IV

show that only a small portion is destroyed by this reagent. Evidence derived from titrations [4, 5] indicates that no considerable number of carboxyl groups of cystine in wool can be free (Formula III) since the number of free carboxyl groups is essentially accounted for by the content of glutamic and aspartic acids. While these data do not afford complete proof, they strongly indicate that all the functional groups of all the cystine are combined, and that only a small proportion, if any, can be free.

On the basis of these considerations at least the major portion of the cystine must form parts of either two separate polypeptide chains (Formula IV) or of a single folded polypeptide chain, and in either case its disulfide group would serve as a connecting or a cross link. Astbury and Street[6] were the first to suggest that such disulfide cross-linkages were present in wool protein; since then Astbury, and Speakman, with their collaborators, have extended this hypothesis.

This view suggests that modification of the mode of linkage of the sulfur in wool should lead to profound alterations in the properties of the fiber. Unfortunately, since many of the processes known to affect disulfide linkages, such as the action of light, of alkalies, and of oxidizing and of some reducing agents, involve side reactions with other groups in the protein, conclusions based on their use may be open to criticism. The action of a few reducing agents, however, appears to be solely with the disulfide groups and therefore it appeared possible to use these reagents in evaluating the relation of the disulfide groups to the structure and properties of the wool fiber. Of these reagents, only thioglycolic acid and certain other mercaptans can reduce each disulfide group to two sulfhydryl groups. Other reagents, such as potassium cyanide, sodium sulfide and sodium bisulfite react with disulfide groups to form not only sulfhydryl groups but others as well[7].

Goddard and Michaelis[7, 8] found that strongly alkaline solutions of thioglycolic acid rapidly converted the disulfide groups of wool to sulfhydryl groups, and that under these conditions, rapid dissolution of the wool occurred. These authors used alkaline solutions since they observed that wool was not dissolved by neutral or acid solutions of the reagent, an observation that led them to conclude that wool could be reduced only at a pH of 10 or higher. Such a conclusion is not compatible with the behavior of disulfides in general, which are known to be readily reduced over a wide range of pH values. In the present investigation, it is shown that the disulfide groups of wool can also be reduced by thioglycolic acid over a wide range of pH, and that if the reduction is carried out in neutral or acid solutions, the fibrous structure of the wool is not destroyed. The use of neutral or faintly acidic solutions of the reducing agent also has the advantage of eliminating such secondary reactions as degradation of cystine, cysteine, peptide, or other linkages.

Wool that has been reduced in neutral or acid solution can be further modified without loss of fibrous structure by treatment with alkyl halides, which convert the sulfhydryl groups to thioether groups*. The reactions may be represented as follows:

(1) $W—S—S—W + 2HS—CH_2—COOH \rightarrow 2W—SH + (S\text{-}CH_2—COOH)_2$

(2) $W—SH + RX \rightarrow W—SR + HX$

where W represents the portions of the wool connected by the disulfide groups, R represents an alkyl group, and X, a halogen atom. Reactions of this type result in the permanent rupture of covalent cross-linkages. Wool fibers have been prepared in which the mode of linkage of at least 95 per cent of the cystine has been modified through these reactions.

Dihalides are also capable of reacting with the reduced wool, the reaction being represented by the following equation:

(3) $2W—SH + (CH_2)_n X_2 \rightarrow W—S—(CH_2)_n—S—W + 2HX$

The reaction with the dihalides results in the formation of new cross links† in which the sulfur atoms of the cystine are connected by short hydrocarbon chains.

The reactions in eq. 2 and 3 offered a means of preparing a large number of wool derivatives. Thus, it was possible not only to investigate the nature of the sulfur linkages and their relation to the structure of the fiber but also to study the effects of introducing into the fiber new groups having widely different properties.

*Goddard and Michaelis [7, 8], and Pillemer, Ecker and Wells[9, 10] also found that their amorphous wool protein derivative could be alkylated by treatment with alkyl monohalides to form other amorphous protein derivatives.

†Speakman[11] has suggested that divalent metal ions, such as that of barium, can form cross-linkages between sulfur atoms. Such linkages would be ionic and unstable, as compared with completely homopolar linkages formed according to eq. 1 and 3.

II. EXPERIMENTAL PROCEDURE

1. Materials

The wool fibers used in the present study were part of the lot used in earlier investigations reported from this laboratory[12]. This material had been subjected to no mechanical or chemical treatment other than successive extractions with alcohol and with ether at room temperature for 5 hours each, followed by washing with water at 40° C.

Worsted yarn was also used for some experiments. It was prepared from raw wool that had been previously extracted with Stoddard solvent and washed with water. The yarn was further purified by extraction in a Soxhlet apparatus with alcohol and with ether for 6 hours each, and finally washed with distilled water.

2. Methods

a. Reduction of Wool with Thioglycolic Acid

Aqueous solutions of thioglycolic acid were used, and were adjusted to the desired pH by adding potassium hydroxide solution. The final concentration of thioglycolic acid was determined by titration with standard iodine solution[13]. It was found advisable to cool the thioglycolic acid solution in an ice bath during addition of the potassium hydroxide, since at higher temperatures the solutions often became colored. Although aqueous solutions of thioglycolic acid were used in all experiments reported in this paper, solutions of the reagent in organic solvents were also found effective.

The reduction was carried out by immersing a known weight of wool in a solution of thioglycolic acid at the required temperature, pH, and concentration. Wetting the wool was facilitated by evacuating the vessel with a filter pump. After the reduction had been allowed to proceed for the desired length of time, the wool was removed and washed several times with distilled water to remove excess thioglycolic acid and its oxidation products

b. Reoxidation of Sulfhydryl Groups of Reduced Wool

Before the reduced wool was reoxidized, it was first washed thoroughly with 95 per cent ethyl alcohol. Omission of this step led to products that contained amounts of sulfur in excess of that in the untreated wool, presumably by the formation of a mixed disulfide, one-half derived from cysteine, the other half from thioglycolic acid. The wool was then rinsed with distilled water, placed in 0.1 *M* potassium phosphate buffer solution at pH 7.0, and a stream of oxygen bubbled through the solution until the wool no longer gave a positive nitroprusside reaction[14]. Finally the wool was again washed with distilled water, and dried in a stream of air.

c. Alkylation of the Sulfhydryl Groups of Reduced Wool

Reduced wool that was to be alkylated was transferred immediately after washing to a 1.0 *M* phosphate buffer solution at pH 8.0, in which had been dissolved or suspended the desired alkylating agent. The rate of alkylation was increased by agitation of the mixture, particularly when the alkylating agent was not completely soluble.

Ordinarily, 0.002 mole of alkylating agent and 100 ml. of buffer solution were used for each gram of wool. The reaction was allowed to proceed until a negative nitroprusside test for sulfhydryl groups in the fiber was obtained.

The reactions take place not only in aqueous buffer solutions but also in organic solvents in the presence of soluble or insoluble substances capable of removing the acid formed in the reaction. For example, solutions of reagents in 50 per cent aqueous methanol, 0.05 *M* with respect to NH_4OH and 0.1 *M* with respect to NH_4Cl, or in benzene in the presence of sodium bicarbonate, were found to be satisfactory.

d. Analytical Methods

The extent to which the sulfhydryl groups of the reduced wool had been alkylated was determined by analyzing the wool for cystine by the Sullivan[15] procedure, as previously used in this laboratory[16]. Neither thioglycolic acid nor thioethers derived from cysteine affect the color reaction of the cystine under these conditions. The adequacy of this method of determining the amount of reaction was checked in certain cases by alkylating the reduced wool with *p*-chlorobenzyl chloride, a reagent that introduces an atom of halogen for each sulfhydryl group with which it reacts. For example, one product that contained 2.2 per cent of chlorine (0.00063 equivalent per gram), also was found to contain 4.7 per cent of cystine. The original wool contained 12.4 per cent of cystine, so allowing for the increase in weight due to introduction of *p*-chlorobenzyl groups during the reaction, the product contained a calculated total of 11.4 per cent of reacted plus unreacted cystine. By subtracting the 4.7 per cent of unreacted cystine from this total, it is seen that 6.7 per cent or 0.00056 equivalent of cystine in each gram of wool had reacted. The amount of halogen introduced therefore corresponds, within analytical error, with the decrease in cystine content of the wool.

The amount of halogen was determined by the Pregl bead-tube method[17]. Sulfur determinations were made by the oxygen-bomb method[18].

The hygroscopicity* of the wool was determined by keeping air-dried samples in a room at 21° C. and 65 per cent relative humidity for 24 hours, and determining the loss in weight on drying in a vacuum oven at 105° C. for 2 hours. The values are calculated as percentages of the dry weights.

Alkali solubility was measured by the method of Harris and Smith[19]. Samples were treated with 0.1 *N* sodium hydroxide solution for 1 hour at 65° C., and the percentage loss in weight was determined.

e. Determination of Physical Properties of the Wool

Two tests were utilized in determining the changes produced in the physical properties of the fiber during the various treatments. The first involved the measurement of the breaking strength of treated yarn by the single-strand method on a pendulum-type machine. The values reported are the averages of 10 or more determinations.

In the second test, the stress-strain characteristics of individual fibers were determined by the method described by Sookne and Harris[12]. This method, which is a modification of procedures used by other investigators†, is much more sensitive to small changes and has greater accuracy than methods involving a determination of the breaking strengths. It is based upon the observation of Speakman[5] that when a wool fiber is immersed in water and stretched under load until it has been elongated 30 per cent, it will return practically to its original length when the load is removed. If the fiber is allowed to relax in the unstretched state in water for about 24 hours, and then again stretched exactly as before, it is found that the same amount of energy (within about 1 per cent) is required to stretch the fiber the second time. If the fiber after the first stretching is subjected to chemical treatments which break chemical bonds, less energy will be required to stretch it the second time. The ratio of the energy required to stretch the fiber the second time to that required the first time is called the *30 per cent index*. It follows that if the 30 per cent index is less than 1, the fiber has been weakened by the treatment; if it is greater than 1, strengthened. The accuracy of this method depends on the fact that comparisons are always made between successive measurements on the *same* fiber. Since wool fibers are extremely irregular and vary considerably in shape and cross-section, comparisons between different fibers would give rise to large errors, which could be only partially eliminated by the application of statistical methods to measurements on large numbers of fibers. With the present technique, as few as 3 fibers were found sufficient to provide adequate checks.

3. RESULTS AND DISCUSSIONS

1. The Course of the Reduction Reaction

The reaction of wool with thioglycolic acid under a variety of conditions was investigated, and is described in the following sections.

a. Effect of pH

Preliminary work showed that solutions of thioglycolic acid to which no alkali had been added reacted with wool, and resulted in the production of sulfhydryl groups, which gave a positive nitroprusside reaction, and were capable of reacting with alkyl halides. These reactions proceeded without destruction of the fiber, whereas strongly alkaline solutions (pH 11.0 or above) of the reagent reacted with the wool, not only to reduce it, but also to dissolve it[7, 8].

The effect of various pH values was studied in greater detail by reducing several samples of wool with a 0.2 *M* solution of thioglycolic acid solutions at 35° C. for 20 hours at various pH values, then alkylating with *p*-chlorobenzyl chloride, and finally determining the amount of unchanged cystine. The results are shown in Figure 1.

*Hygroscopicity is used here in an arbitrary way. Actually, the amount of moisture absorbed by wool will vary both with temperature and relative humidity.

†For literature citations see [12].

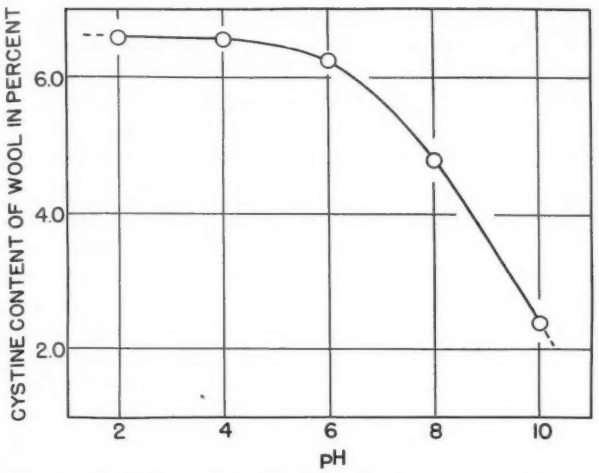


Fig. 1—Cystine content of wool after reduction at various pH values for 20 hours at 35° C. with 0.2 *M* thioglycolate solutions, and alkylation with *p*-chlorobenzyl chloride.

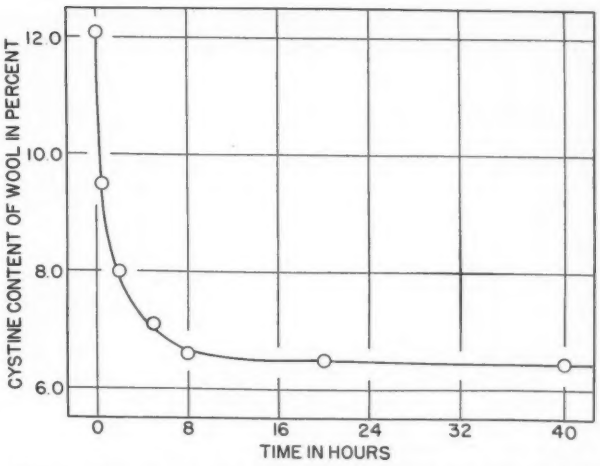


Fig. 2—Cystine content of wool after reduction for various lengths of time at pH 4.5 and 35° C. with 0.2 *M* thioglycolate, and alkylation with *p*-chlorobenzyl chloride.

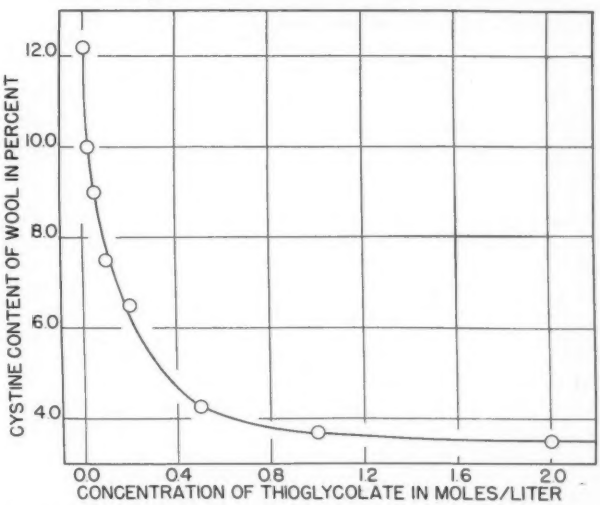


Fig. 3—Cystine content of wool after reduction with thioglycolate solutions of various concentrations for 20 hours at pH 4.5 and 35° C., and alkylation with *p*-chlorobenzyl chloride.

It will be noted that the amount of reduction was practically constant over the pH range of 2 to 6, somewhat greater at pH 8, and very markedly greater at pH 10. The decrease in cystine in the alkaline region is due not to destruction of cystine by alkali but to reduction, since wool that has been reduced for short periods (2 hrs.) under these conditions can be reoxidized to products containing nearly the original amounts of cystine and sulfur. Longer exposure (20 hrs.) of wool to thioglycolic acid at pH 10 resulted in material that contains an abnormally low amount of cystine after reoxidation, but because a considerable portion of the wool was dissolved under such conditions, the results were probably caused by extraction of cysteine-rich material. The increased reduction in alkaline solutions may be caused by ionization of sulfhydryl groups. This could change the mechanism of action of the reducing agent, and also, ionization of sulfhydryl groups formed in the wool itself would increase swelling and facilitate penetration of the reagent.

Wool reduced in acid solution maintained its original appearance, but wool reduced at pH values of 9.0 or above became gelatinous when wet, and brittle and resinous when dry.

b. Effect of the Duration of the Treatment

The amount of cystine reduced during treatment of wool for various lengths of time with 0.2 *M* thioglycolic acid at pH 4.5 and 35° C. is shown in Figure 2. Under these conditions the reaction proceeded to about one-half of its final extent in the first 2 hours and to about 95 per cent of its final extent in 8 hours.

c. Effect of the Concentration of Thioglycolic Acid

The amount of cystine reduced in 20 hours at 35° C. and at pH 4.5 by various concentrations of thioglycolic acid is indicated in Figure 3. Sufficient reducing reagent to insure the presence of at least 20 times the amount of thioglycolic acid theoretically necessary to reduce all the disulfide groups of the wool was used in each experiment. The amount of reduction increased rapidly in the range 0.01 *M* to 0.2 *M*. The effect was less marked between 0.2 *M* and 0.5 *M*, while increasing the concentration of thioglycolic acid beyond 0.5 *M* had little further effect.

d. Effect of Temperature

The amounts of cystine reduced during treatment of wool for various lengths of time with 1.0 *M* thioglycolic acid at pH 4.5 and at 10° C. and 50° C. are shown in Figure 4. At 50° C., the reaction was essentially complete after 1 hour, while at 10° the reaction proceeded more slowly. Increasing the temperature, however, did not increase markedly the amount of cystine finally reduced.

2. Alkylation

Most of the alkyl halides that were investigated were found to react more or less readily with reduced wool. In general, the reaction took from 6 to 24 hours at 35° C. to reach completion, depending on the amount of reduction of the wool and on the reagent used. It was found that iodides reacted faster than bromides, and bromides faster

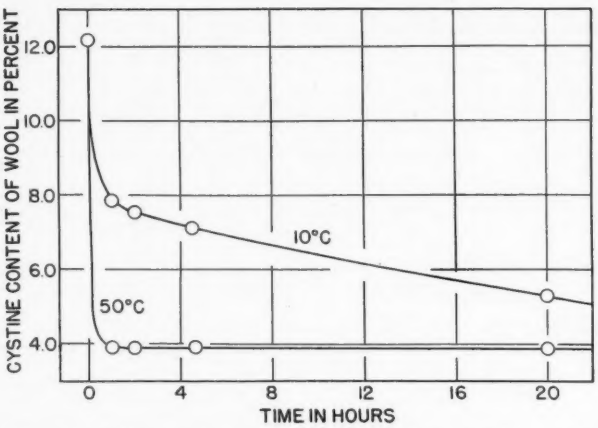


Fig. 4—Cystine content of wool after reduction with 1.0 *M* thioglycolate at 10° C. and at 50° C. at pH 4.5 for various lengths of time, and alkylation with *p*-chlorobenzyl chloride.

than chlorides. Tertiary alkyl halides, such as tertiary butyl chloride and triphenylmethyl chloride, were found to be almost completely unreactive.

Besides the reagents listed in Table 1, the following were also found to be reactive: allyl chloride, 2-methylallyl chloride, chloroacetone· methyl chloromethyl ether, ethyl chloride, ethylene dichloride, 1,3-dichloroisopropanol and 1,3-dibromoisopropanol. Ethylene oxide and epichlorohydrin were also found to react with the sulfhydryl groups of reduced wool.

3. The Properties of Reduced and Alkylated Wools

The properties of wool fibers and yarn that had been modified by reduction and alkylation are summarized in the following sections. In each instance, the wool was reduced for 20 hours at 35° C. and pH 4.5 with a large excess of 0.2 *M* thioglycolic acid. Duplicate experiments were found to lead the variations amounting to less than 0.02 in the 30 per cent indices, 0.3 per cent in hydrations, and 0.5 per cent in alkali-solubilities. Analyses showed that the materials contained 6.5 ± 0.5 per cent of cystine in every case; that is, the mode of linkage of approximately half of the sulfur atoms had been altered, since the untreated wool contained 12.4 per cent of cystine.

(*a*) *Physical Properties*

As indicated by Table 1, the breaking of cross-linkages during reduction greatly decreased the 30 per cent index of the fibers. Reduction followed by reoxidation resulted in the restoration of nearly the original 30 per cent index, indicating practically complete reaction of the sulfhydryl groups to rebuild disulfide cross-linkages. Fibers modified by reduction followed by alkylation with an alkyl monohalide of low molecular weight, such as methyl iodide or ethyl bromide· were only slightly less easily elongated than those reduced alone. Alkylation with chloroacetic acid introduced ionizable carboxyl groups (combined as —S—CH_2COOH) into the fiber. The data show that wool fibers treated in this manner have 30 per cent indices of the same order as those of wool fibers reduced alone.

TABLE 1

Thirty per cent indices and breaking strengths of wools reduced and alkylated with alkyl monohalides.

Treatment	*30 Per Cent Index*	*Breaking Strength*
		Grams
Untreated	0.99	1310
Reduction	0.65	1170
Reduction and reoxidation	0.97	1310
Reduction and CH_3I	0.67	1190
Reduction and C_2H_5Br	0.70	1250
Reduction and $C_6H_5CH_2Cl$	0.92	1310
Reduction and p-$ClC_6H_4CH_2Cl$	0.95	1450
Reduction and $C_7H_{15}Br$	0.95	1380
Reduction and $C_{12}H_{25}Br$	0.96	1340
Reduction and $ClCH_2COOH$	0.67	1240

Reduction of wool followed by alkylation with monohalides of higher molecular weight, such as benzyl chloride, *p*-chlorobenzyl chloride, heptyl bromide, or dodecyl bromide gave products higher in 30 per cent index than those obtained with methyl iodide or ethyl bromide. Such behavior appears to be due either to the action of intermolecular forces of the van der Waals type between alkyl groups on neighboring sulfur atoms, or between these groups and other parts of the polypeptide chains of the protein. Such secondary linkages would be expected to be weaker than the original covalent type. The data in Table 1 offer suport for such a hypothesis

When aliphatic dihalides are used to alkylate reduced wool, groupings that may be represented as W—S—$(CH_2)_n$—S—W appear to replace the disulfide bridges of the original wool, as eq. 3 indicates. Analogous reactions of dihalides with simple mercaptans are known[20], and evidence that the reaction proceeds in this way is found both in the properties of the products, and in the fact that they are practically free of halogen. The halogen contents of several samples of wool prepared by reduction and alkylation with trimethylene dibromide are shown in Table 2. Included in the table are halogen contents

TABLE 2

Bromine content of wool reduced and alkylated with trimethylene dibromide.
Calculated results are based on the assumption that only one bromine atom of each dihalide molecule has reacted.

Cystine Reacted	*Bromine Calculated*	*Bromine Found*
Per Cent	*Per Cent*	*Per Cent*
2.1	1.6	0.1
6.4	5.0	0.1
8.4	6.5	0.0
10.2	7.9	0.2

calculated on the basis of the assumption that only one of the bromine atoms of the dihalide had reacted. It is readily seen that only a very small fraction of the dihalide molecules had reacted in this way. Extensibility of the wool prepared in this way would be expected to be slightly increased, presumably since the cross-linkages between polypeptide chains would be lengthened, and it should increase further as the number of methylene groups separating the two sulfur atoms is increased. The data obtained with fibers reduced and treated with methylene

(Continued on page 447)

PROCEEDINGS OF THE

American Association of Textile Chemists and Colorists

AUGUST 18, 1941

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CALENDAR OF COMING EVENTS

Annual Meeting and Convention, Carolina Hotel, Pinehurst, N. C., Oct. 31, Nov. 1, 1941.

PIGMENT PRINTING PROBLEMS*

E. P. SOMMER
General Dyestuff Corp.

THE application of pigment colors on textile surfaces as you all know is something very old. In fact centuries ago the only means of surface decoration consisted of painting mineral pigments on textiles or leather garments until the better wearing fastness of vegetable dyes on mordant preparations became general knowledge of human society. But even after the invention of the modern groups of synthetic dyestuffs, the use of Ultramarine Blue and Pigment Black for special purposes, never has been given up entirely.

Some of these old pigment preparations when mixed with the help of a good grinding mill, thickened with animal glue and aged with formaldehyde fumes were surprisingly fast for those times. The mentioning of formaldehyde fumes in connection with animal glue shows us the first application of artificial resin for fixing a pigment on a textile surface. The polypeptides of the animal glue so to speak are organic amines which with formaldehyde combine to a water resistant resin in a way similar to urea and formaldehyde. Roasted British gum and gum Arabic had been used as extender and thickening agent in combination with animal glue, and prints with excellent sharp mark could be obtained by this method. Glycerine and olive oil were added as plasticizers, and in old recipes one can read that never more than 5 per cent oil should be added since otherwise the crocking fastness would be too bad. In order to improve the stability of the printing paste ammonia was added.

Here you have again the case that the old-timers observed certain rules in their practical work without knowing anything about theories. Today we take it for granted that proper pH control has to be applied when making up pigment preparations or resinous combinations. In other words either the stability of the pigment printing paste is too limited when working at too acid a pH or the polymerization of the resin solution or resin dispersion is retarded when working at too high or alkaline pH value, thus resulting in impaired soda-soap fastness.

Coming back to our old-time pigment printing method I really don't know how old the application of pigments fixed by means of animal or vegetable glues and formaldehyde fumes is; however, I am certain that it is much older than most of us here in this room. Some years ago this method was revised to a large extent when printing white pigment effects with egg-albumen and adding the formaldehyde right to the printing paste in the form of hexamethylene-tetramine. In some instances the pigment white was tinted in pastel shades by adding suitable direct colors and urea, mostly for fancy styles on lustrous textile surfaces.

The main drawbacks of this old pigment printing method were: moderate crocking fastness of the pigment, high price, and poor stability of the thickener and binding agent, and finally a certain stiffness and boardiness of the printed cloth which could not be fully overcome by addition of glycerine and plasticizers.

So you might ask, why dig out those old stories since we have something quite different in mind when speaking in terms of pigment printing today. Well, the reason for doing so is that in my opinion many of us have lost sight of the fact that pigment printing today is nothing basically new but rather the streamlining, simplifying and improving of something which has been buried long ago in the old records of many printing mills. While some of us believed that a new era of textile printing was ahead it was quite evident to other men brought up in textile research that the crocking fastness in certain medium and in many heavy shades at the present stage of pigment printing would not be good enough when printing large coverage for better fabrics with higher fastness requests. Furthermore those of us who know how difficult it is sometimes to obtain a good scrubbing fastness in certain piece dyed shades on certain fabrics, realized right from the beginning the difficulties possibly involved with pigment printing. Whereas all the new pigment printing methods produce prints of excellent soda-soap fastness even when submitting to a 2½ hour laundry test at 180° F., scrubbing with concentrated cold soap solution very often shows the pigment prints to be rather deficient. For this latter reason most of the better grade shirtings are still being printed with vat colors, though the crocking fastness perhaps might be good enough because shirting patterns consist mostly of light pastel shades, having darker colors only in small peg objects or in fine lines.

There are certainly millions of yards of shirtings and shorts being printed with pigments, but not for high-grade fabrics.

Speaking about shirtings brings us to the problem of sharp mark, which supposedly can be obtained much better

*Presented at meeting, Rhode Island Section, April 25, 1941.

with pigment printing preparations than with the other dyestuff classes of the chemical fixation type. A sharp definition of the printed design without question can be obtained easier and cheaper with pigment colors either of the emulsion type or of the water dispersible brand; but it is utterly wrong to claim that only blurry outlines can be obtained with the conventional printing methods. I think the excellent quality of shirtings which are printed right here near Providence proves my argument.

Plenty of starch for pigments or for vats or Rapidogens is certainly very economical but certainly just as bad for the furnishing quality of printing pastes. For higher requests more money has to be paid for the printing carrier. This is also the case when printing with the oil emulsion type of pigment paste.

Our own research work on water dispersible pigment preparations has taught us the stabilizing and printing qualities of methylcellulose solutions which now are available at a really cheap price. The drawback of methylcellulose in combination with aqueous resin carriers plus some starch is the decreased color yield with certain pigments. We are running trials with new brands of sodium alginate of excellent stability and very good color yield for aqueous pigment preparations. I shall talk about these problems in more detail later.

For the time being it might be sufficient to mention all these factors merely to show that pigment printing taken seriously as a technical problem, and far away from all sales talk, is a highly complex affair, whereby it is very dangerous to generalize in sweeping statements for the sake of giving preference to one or the other method. All research work in modern pigment printing is of recent date, and a really foolproof and perfect pigment printing method has yet to be found. Many laboratories, including our own, are busy on this problem. Very likely the whole race will wind up with several methods, both for the cheapest possible effect with fairly good properties, and also for the highest possible requests at a somewhat higher price.

Without question the present pigment printing methods are already far advanced, whereby one should not fail to give credit to those men who were the first to visualize the new possibilities which have been made available with new resins, new solvents, plasticizers, emulsifiers, etc., in connection with textile printing. The reasons for the exhaustive research work in pigment printing (despite its shortcomings) are its two big advantages in the application of pigments.

(1) Much quicker production due to elimination of after-treatments (except soaping).

(2) Less seconds, mainly for the same reason, but also due to the fact that pigment colors are so much better visible for the printer at the machine.

Another point in favor of pigments is that new pigment brands have been brought on the market recently, of excellent shade and outstanding light fastness. For example, the copper phthalocyanines, which cannot be matched as regards shade or light fastness, even not when resorting to vat colors; also some of the grey, brown, and yellow shades in the pigment range are unsurpassed as regards light fastness.

It is safe to say that the pigment colors have their merits, and therefore again a definite place among the various lines of textile printing colors, although the textile trade today sees also their limitations and defects at least in their present stage of development.

As mentioned before, pigment printing technically is a very complex problem.

The full yield and shade of the pigment color has to be developed before stirring the pigment preparation into the printing carrier. You cannot just use a pigment powder and mix it with your printing carrier. Even a good mill alone will not do. You might obtain some results, but as soon as you check more carefully you will find that you lose brightness or color yield or crocking fastness or all these factors together.

Furthermore each new resin-combination has to be tuned up to your pigment preparation or vice versa. In addition the extender has to be well balanced towards both pigment preparation and resin combination, as long as you are striving for optimum results.

After doing all this you might arrive at a formula which works nicely in the laboratory, but the printing pastes might break when running at high speed in the machine.

. . . (Demonstration of laboratory prints and plant prints) . . . So after all only practical mill runs are the real test for the merits of a pigment-resin concoction.

The above comparison of laboratory prints, which show a certain dispersion to be so effective in the laboratory, simply proves that dispersion of a pigment is not enough for practical conditions. In other words the pigment preparation has to be stabilized and, so to speak, insulated towards static electricity and strenuous crushing effect as well as shearing strain which takes place in a big printing machine and which cannot be duplicated when running a small laboratory machine at slow speed.

However, before looking more thoroughly into certain phenomena of pigment dispersions we ought to get a clear picture as to what principles of pigment printing are used today.

As you all know, the first of the modern pigment printing methods was based on an oil emulsion printing carrier. I might say right in the beginning that so far as a color yield is concerned, the oil emulsion type of resinous printing carrier works very satisfactorily. In speaking of oil emulsions, we have to distinguish between water in oil emulsion, and oil in water emulsion.

In the case of the water in oil emulsion, the oil is in the outer or the continuous phase. Therefore, when stirring more water into such an emulsion by means of a high speed stirrer, a thickening of the emulsion takes

place. In other words, the water itself works as a thickening agent. The drawback is that such an oil emulsion is not miscible with other aqueous printing gums. The advantage is that due to the utilizing of the false thickness obtained by adding water a rather cheap printing carrier can be obtained.

In the case of an oil in water emulsion the oil is the inner phase and the water represents the outer continuous phase of the emulsion. Such an oil emulsion is miscible with aqueous preparations; it requires, however, oil as a thickening agent and is therefore more expensive.

When working with an oil emulsion printing carrier we can utilize the higher affinity of pigment colors towards oil for developing the full pigment shade in the form of a pigment emulsion. I mean to say that all pigments have a much higher affinity to oils or to certain solvents of oily character than to water. We all know that most of the painting of our houses on the outside is being done with oil paints, although recently so-called water paints have been brought out on the market mainly because water paints fixed with certain water soluble resins dry much quicker and give nowadays about the same fastness as oil paints. At any rate, generally speaking, the pigment colors, due to the higher affinity towards oil, can be developed much quicker, or at least easier in oil medium than in aqueous bases. This higher affinity of pigments towards oil or oily solvents can be illustrated very simply right here by this little demonstration.

. . . (Demonstration of oil flushing of pigments) . . .

You will see that practically all the pigment of the pulp has been extracted from the aqueous suspension and we then have the pigment after short stirring in an oil medium. If you grind this pigment oil cake on suitable mills, adding some solvents and oil soluble resins with some suitable emulsifier, then stirring some water into the oily preparation, you have a pigment preparation of the oil emulsion type, which then can be intermixed with an oil emulsion resinous printing carrier having if necessary also some resin in the oil phase of the cold-cream-like printing paste.

In other words both the pigment and the resin are in the oil phase of the emulsion, which then is brought to the right concentration by emulsifying more water or oil into this preparation, depending on the viscosity which is required.

As mentioned before the advantage of this oil emulsion type of pigment printing preparation is the ease with which full and bright shades can be developed and the fairly cheap price. The drawback is, as also mentioned before, that such a preparation, having both the pigment and the resin in the oil component, cannot be intermixed with aqueous printing gums or with water, at least unless one is using the high speed mixer for obtaining emulsification.

Of course nobody would think of mixing pigment printing pastes of the oil emulsion type with aqueous printing gums. I mean nobody would do such a thing on purpose. The sad story is, however, that this actually does take place when printing pigment shades of the oil emulsion type alongside Rapidogens, Fast Color Salts or Aniline Black. As you know, it simply cannot be avoided that some amount of the pigment printing paste runs into the neighboring color box by means of the usual carry over, or as it happens sometimes, one printing paste passes by one or two printing rollers and suddenly for unknown reasons is picked up by the following third roller. Many printers have scratched their heads to find an explanation for some of these phenomena; why one gum passes one or two rollers to be picked up all of a sudden on the third one. I think it is a mute question to form theories, particularly when switching the rollers does not help at all. At any rate, as long as a pigment printing paste is constructed in such a way that it is intermiscible with aqueous printing gums which have been used for thickening up water soluble colors, not much damage can be done except perhaps some dulling of certain shades. However, when a pigment preparation is not miscible with aqueous gums, a building up on the neighboring rollers or a scumming under the doctor blades might occur.

There is apparently quite some variety of opinion as to the extent of these difficulties when printing oil emulsion carriers alongside aqueous dyestuff pastes. Some friends have told me that they have no difficulty at all in this respect, whereas other plants apparently do have trouble on that score. Various additions either to the pigment paste or the Fast Color Salt printing paste have been offered. All these troubles, of course, could be eliminated easily when having only pigment preparations of the oil emulsion type in the printing pattern. This, however, is not possible, since the usual very heavy and bright red, maroon, and navy shades of the azoic type, cannot be obtained with the same strength and richness when resorting to pigment preparations. To a certain extent it is possible; however, the crocking fastness in this case is so bad that the printed goods can hardly be considered as salable merchandise. Besides this, Fast Color Salts printed on Naphtol As preparation are so cheap that they cannot be nearly approached as regards price by any pigment preparation. Another way out might be to print the Fast Color Salts with an oil emulsion printing carrier. Some trials on this order have been conducted, however, without definite results as yet.

Another possibility to escape this dilemma is to work entirely in the opposite direction and to develop a pigment printing procedure which is based on a print paste having both the pigment and the resin in an aqueous medium. Just in recent months we have witnessed some new developments on this order, and to the best of my knowledge at least four different aqueous resin preparations are on the market which all have certain merits. My personal opinion is that aqueous pigments and aqueous resin compositions will find more and more consumption

in the textile trade. The only exception might be the pigment printing on flannels or other fabrics with a napped surface in which case the oil emulsion type of printing carrier, due to the very low solid content of this vehicle, is without question superior to the aqueous resin dispersions which are known at present.

The relatively higher solid content of the aqueous dispersed type of pigment printing paste is not caused so much by the water soluble or water miscible resin itself but more so by the aqueous printing gum solution or starch paste which is applied in connection with the resin solution for obtaining sufficient viscosity of the printing paste.

In other words, three major items have to be considered when working with an aqueous pigment printing preparation: (1) The pigment preparation itself, which exists either in the form of an aqueous pulp or of a water miscible pigment ink. (2) The water miscible resin solution or dispersion. (3) The printing gum which has been used as an extender for obtaining the necessary viscosity as explained above.

As I have already said before, all three major components have to be adjusted in such a way that the highest degree of intermixing and dispersion takes place by means of simple hand stirring. Due to the great variety of resin modifications as well as to the great number of printing gums or starches, there are numerous ways possible for obtaining this goal. Things become quite complicated insofar as almost each pigment behaves differently. Some pigments work very well with certain dispersing agents when combining with a given resin preparation, whereas other pigments have to be dispersed in a different way again when they are to be intermixed with the same resin solution and still maintain the same printing gum as an extender. This is the reason why in the beginning I said that pigment printing is a highly complex affair and that it is very dangerous to generalize with sweeping statements for the sake of giving preference to one or the other method.

At any rate, whatever the dyestuff manufacturer has to do to make a certain pigment workable with an established resin formulation is not the worry of the textile printer. He simply takes it for granted that the pigment works in a more or less foolproof way with any aqueous resin formulation which he happens to have on hand. All that the textile printer asks for is that the pigment be well dispersed and give full wash fastness and the highest possible crocking fastness with his established plant procedure.

As to the water dispersibility, we might resort again to a short demonstration showing the fundamental difference of a water dispersible pigment compared with a pigment—oil—emulsion.

. . . (Demonstration) . . .

Such a pigment preparation in water miscible ink form contains not only the dispersed pigment but also sufficient grinding vehicle, which at the same time is necessary for giving sufficient bondage between the pigment itself and the textile surface. Besides this, solvents are added for giving a lubricating effect to the finished printing paste and for stabilizing the pigment dispersion itself towards the mechanical churning strain to which the pigment dispersion is subjected while running in the printing machine. For higher fastness requests it might sometimes be advisable to add some resin to the printing gum, the amount of which to some extent depnds on the pattern. For larger coverage a somewhat higher resin concentration is advisable than for smaller peg objects, because the weak spot of all pigment printing, as mentioned in the beginning, is the comparatively inferior fastness to scrubbing; and naturally, defects after a cold hand soaping are more visible in patterns showing single objects in large coverage.

For insuring the good stability of an aqueous printing paste during the storing in the color shop, it is advisable to keep both the pigment preparation and the resinous combination slightly on the alkaline side. The curing of the resin during the drying or baking operation can be achieved easily by adding ammonium sulfocyanide or other acid splitting ammonium salts to the printing paste. We have studied this problem carefully and find that printing pastes with a pH value of about 7-8 give excellent stability, and when splitting the ammonium salt at elevated temperature, the pH value drops very fast to about 5 or even somewhat lower, thus effecting the polymerization of the resin.

Other procedures work somewhat differently insofar as they apply the pigment in the form of a simple aqueous pulp having all the necessary resin only in the printing gum preparation. Such a procedure has one big advantage: cheap price. There is a certain drawback as far as we can see it now: as mentioned above, the pigment dispersion has to be tuned up to the resin-starch or gum combination in order to obtain optimum results, particularly as regards running properties. As you probably know, some pigments have a distinctive influence on the physical properties of the vehicle to which they are added, so that certain pigments are apt to run drier or to scum easier under the doctor blade than other pigments. These difficulties caused by the individual properties of pigments can be eliminated by subjecting the pigments in combination with a grinding vehicle and water miscible solvents to a mechanical treatment, whereafter all pigments, so to speak, emerge in a uniform physicochemical state.

In this connection I have to show you a number of practical prints.

I first show you some patterns of the conventional dressgoods style, showing the pigments in smaller objects, and also Fast Color Salts or other azoic colors in scattered designs. We hardly experience any trouble when running such patterns with ordinary aqueous pigment pulps. On the other hand when having both the pig-

ments and the Fast Color Salts in large coverage, we find it quite frequently to be very difficult to avoid picking up the pigment print impression on the Fast Color Salt printing designs or vice versa, or in some instances the pigments scum into the Fast Color Salt blotches. We have run large scale trials of inks comparatively with aqueous pulps, showing that under otherwise equal conditions the inks run without trouble, whereas the aqueous pulps either run dry or snap or scum under the doctor blade, resulting in defective prints.

These prints were done some time ago and it is possible that there are today aqueous resin combinations on the market which behave much safer in this respect in combination with aqueous pigment pulps.

There is one problem for me still to discuss: namely, the influence of the printing gum which has been used as an extender. Starch naturally, as in the case of the chemical fixation type of dyestuff, gives the strongest color yield. The drawback as we see it is boardiness, and a certain lack of smooth coverage, which perhaps goes parallel with a certain short viscosity of the finished pigment printing paste. It appears to me that in the case of pigment colors a flowing consistency of good length is more important than in the case of water soluble printing dyestuffs for insuring optimum running properties in the machine, which is particularly necessary for obtaining smooth coverage and absolutely clear printing effects in large objects.

On the strength of large scale trial runs we found that methylcellulose solution in combination with the usual starch brands has a very beneficial effect in printing difficult patterns, preventing pinniness of the Fast Color Salt prints caused by picking up pigment specks or vice versa. Unfortunately methylcellulose solution, due to its peculiar colloidal properties, weakens the color yield of the pigment prints. This colloidal influence of various printing gums is very pronounced, and even more so than it is known from the conventional printing methods of the chemical fixation type.

I am showing you here a laboratory print with 6 stripes, each one containing the same pigment and resin preparation. I think you can see, even from where you are sitting, the tremendous difference between stripe No. 1 and stripe No. 4. The latter shows at least twice the color yield of the first one. The only difference is that one has been printed with a combination of 1 part Colloresine and 2 parts starch, whereas the fuller shade has been printed with a combination of 1 part gum tragacanth and 2 parts starch. Stripe No. 5 has been printed with a combination of 1 part sodium alginate and 2 parts starch and gives about the same excellent yield as the gum trag starch combination. The trouble is that a good gum tragacanth today, if available at all, is very expensive and besides this, printing pastes with gum tragacanth or starch-tragacanth are rather unstable either to storing in the color shop, or when printed at high speed. Some of our trials with sodium alginate in combination with starch, look rather promising.

These trials showing the tremendous influence of the printing gum, leaving all other components constant, prove that pigment printing involves a considerable amount of surface phenomena. Whereas many people believe that due to the elimination of all chemical aftertreatment in the case of pigment printing, much more consistent results are obtained as compared with the chemical fixation type of printing colors, the truth is that the physical standardization of pigment colors is at least as difficult as the coloristic standardization of vat or azoic colors of the conventional textile printing dyes. There is, however, one and very important consolation for you gentlemen of the textile trade and that is that these difficulties do not concern you but rather us alone. Of course you meanwhile are already used to taking dispersed pigment colors in bright shades and with excellent fastness and running properties as a matter of fact. That this has been possible in such a short time is due only to the willing and patient cooperation of certain textile printing mills.

The purpose of my mentioning so many problems in such a scrutinizing way is merely to show that despite all progress, still a lot of work has to be done before we shall have reached the final goal of an ideal pigment printing procedure.

With this purpose in mind, we shall appreciate your further cooperation, as in the past.

OUTING, NEW YORK SECTION

THE annual outing of the New York Section was held on Friday, June 20th, 1941, at the North Jersey Country Club, Paterson, N. J.

The feature of the outing was the golf tournament in which the following were awarded prizes: *members*—low net (cup), Robert A. Scher, 89—20, 69; low gross, D. Rion, 81; kickers handicap (79), E. Freedman, P. Doherr and A. Kellner; *guests*—low gross, tie, E. A. Bush and B. B. Allen, 77; kickers handicap (71), A. Born, M. Hanan, C. Sabriski and H. Toderbush. The bobby prize for the drive nearest the pin on the eighth hole was tied for by H. C. Hennig and G. W. Smith. Paul Duggan was awarded a prize for the largest number of strokes on a hole (13).

Winners in the tennis tournament were Harris Jarrick and Carl Fisher. Awards for proficiency in horseshoe pitching were made to Messrs. Damon, Lovett, Pitt, Henne, Arnold and Garbler.

The outing concluded with dinner and a fine program of entertainment.

The committee responsible for the outing, which attracted a record attendance, was headed by Max Kaesche, chairman, assisted by Paul Luck, George Baxter, Herman Baumann and Robert Holloch.

Respectfully submitted,

NORMAN A. JOHNSON, *Secretary.*

ANNUAL OUTING
NEW YORK SECTION

North Jersey Country Club
Paterson, N. J., June 20, 1941

Photos by N. A. Johnson

ANNUAL MEETING AND CONVENTION

RESERVATIONS

D. Stewart Quern
Chairman, Reservation Committee

D. STEWART QUERN of the Becco Sales Corporation, Charlotte, N. C., and Secretary of the Piedmont Section, has been appointed Chairman of the Reservation Committee of the National meeting of the A.A.T.C.C. to be held in Pinehurst, N. C., October 31-November 1. The following members are assisting Mr. Quern with reservations:

L. M. Boyd, Scholler Bros., Inc., Salisbury, N. C.
R. D. Howerton, Calco Chemical Co., Charlotte, N. C.

A. Henry Gaede, Laurel Soap Mfg. Co., Charlotte, N. C.
J. W. Ivey, Mathieson Alkali Works, Charlotte, N. C.

Hotel reservations should be made direct to Mr. Quern, 1930 Harris Road, Charlotte, N. C.

Rates at The Carolina, headquarters of the association meeting, will be $7.00 per day per person for double rooms, $8.00 per day for single rooms. There are very few single rooms available. Minimum rate for a double room will be $14.00 per day whether room is occupied by one or two persons.

There are other nearby hotels available in case there are more requests for reservations than can be handled in the Carolina. The rate for these other hotels will be approximately $1.00 per day less than at The Carolina.

All requests for room reservations must be accompanied by the names of those who are to occupy the rooms. Reservations for a number of rooms cannot be accepted without the names of those to occupy the rooms due to the fact that the room accommodations of The Carolina will be taxed to the limit, and the committee wants to provide for the greatest comfort of everyone attending the convention.

OCTOBER 31st — NOVEMBER 1st
THE CAROLINA, PINEHURST, N. C.

The Dyeing of MIXED FIBERS IN HOSIERY*

ALFRED J. CARBONE
Sandoz Chemical Works, Inc.

THE dyeing of mixed fibers in hosiery is by no means a new problem to the hosiery dyer. The introduction of new fibers together with fluctuations in the cost of raw materials is making it ever increasingly necessary for the hosiery dyer to keep in step with new developments, and by so doing, disappointing results in the dyehouse are reduced to a minimum.

Because of the large production of full-fashioned hosiery in this territory, my discussion will be confined to this type of hosiery, containing mercerized cotton, rayon and silk, also nylon and silk.

When viscose and Bemberg were first introduced into this country their first attempts to replace silk in hosiery were very disappointing. Gradually the physical properties of rayon were sufficiently improved to create a new interest among the users of silk yarn. Unfortunately many of the direct colors normally used for the dyeing of mercerized cotton and silk hosiery are not satisfactory for the dyeing of mercerized cotton, rayon, silk mixtures. Consequently this helped to postpone the adoption of rayon still further for this purpose. It was only when a shortage of silk threatened, together with an advance in price, about two years ago, that a serious attempt was made to use rayon in admixture with cotton and silk. This made it possible for the manufacturers to maintain their low-priced numbers.

With the demand for rayon yarns, in this new field, regular users in other industries also increased their demands for replacing silk. This resulted in a temporary shortage of certain types of rayon and the use of other types which up to this time had not found any widespread application in hosiery. Some rayons were tried because of their high tensile strength, but these, because of their low-dyeing index, did not offer a satisfactory solution of the problem. Sample stockings were made up and sent to the dyehouse for dyeing. The results, in most cases, were not satisfactory. Repeated requests were received by the dyestuff manufacturers for dyes that would produce a good union between cotton and rayon. It was not an easy matter to satisfy this demand. There are many other factors which must be considered in choosing the proper dyestuffs, such as wash fastness, permanence of color to acid finishing, staining of the silk, level-dyeing, and oftentimes acetate rayon white effects.

*Presented at meeting, Philadelphia Section, May 2, 1941.

In substituting part of the silk by rayon, the double welt was the first to be replaced, thus effecting a substantial saving in silk, without materially altering the stocking in appearance. If rayon and silk are the only fibers present, the dyeing problem is a comparatively simple one. Unfortunately, this is seldom the case. Most frequently mercerized cotton is plaited with silk in the foot, in addition to substituting rayon in the welt, while the silk is maintained in the leg. A fact that complicates things further is that the trade is demanding sheer silk and this necessitates avoiding prolonged dyeing and excessive handling.

Many dyers of full-fashioned hosiery prefer to dye light shades from a soap bath, using direct colors which leave the silk white, or nearly white, and then shade up the silk with acid colors. These acid colors, of course, must be satisfactory for dyeing from an alkaline bath.

Some direct colors which have good rayon dyeing properties and at the same time produce a good union between mercerized cotton and rayon, also dye the silk rather heavily even in an alkaline bath; furthermore they are inclined to gradually transfer themselves to the silk as the dyeing progresses.

In the rapid-dyeing types of rayon, such as the Bemberg, this property of direct colors to transfer themselves to the silk is not nearly so noticeable as in the case of some of the slower-dyeing viscose types. In the dyeing of extremely slow-dyeing viscose which requires larger proportions of direct color than Bemberg, there is danger of going heavy on the silk even without the use of acid color. By changing over to silk white colors this difficulty is obviated.

A slow-dyeing viscose dyes much lighter than the cotton, especially at the beginning of the dyeing operation, but after the dyeing has continued for about one-half hour, after the addition of Glauber's salt, the viscose gradually increases in depth and more nearly approaches the depth of the cotton without, however, actually reaching a good union. In cases where it is impossible to produce a good union if at least the tone of the cotton is the same on both fibers, the stocking will stand a good chance of passing the final inspection.

With reference to the choice of rayon yarn to be used for replacing the silk welt, a semi-delustered yarn seems to produce the most pleasing effect. Heavily pigmented yarns are not only difficult to dye, but do not seem to

blend nicely with the silk leg. When observed from one angle the dyed rayon welt may appear light, when observed from a different angle it may appear much heavier than the silk. In the case of bright rayon yarn, the welt has an undesirable luster which must be removed, but the percentages of duller necessary to do this may result in bringing about a chalky appearance of the silk.

In the dyeing of stockings containing mercerized cotton, rayon and silk, the following procedure has been found to give good results:

The degumming bath is set with part of the direct color, and allowed to boil for about 30 minutes. From 1 to 10 per cent Glauber's salt crystals are then added, the quantity depending on the type of rayon and the depth of shade to be produced. After continuing the boil for 20 minutes longer a sample is taken, dried on the form and examined. Additions of direct color are then made in order to bring the rayon and cotton within a close range of the standard. It is unsafe to add acid color until one is sure that the desired depth of shade on the rayon is under control. Acid color is then added along with the required direct color and the lot is brought to shade. It is advisable to treat the samples with finish before matching off in order to compensate for small changes in shade which may be caused by the acid finish.

It is customary in matching off to pay particular attention to the union between the rayon top and the silk leg, keeping the rayon slightly lighter than the silk, even if the shade of the cotton is slightly off. Uneven plaiting of the cotton and silk in the foot will tend to accentuate small differences in shade.

There is no doubt that the question of finish has had its bearing on the choice of colors for this work. We are of the opinion that the turning down of colors by some dyers as not sufficiently fast to finish was brought about by the necessity of using a more drastic finishing procedure than that formerly required. The desire, for example, of producing a hose which feels altogether like an all-silk hose, makes necessary the use of larger percentages of softening agents than were formerly required on cotton tops. Softeners of the cation active type have been largely used for this purpose, especially in the case of Bemberg, and these too vary in their effects in change of shade of dyestuffs.

In an attempt to secure a good union between rayon and cotton, various expedients have been suggested, such as temperature control at or below 180° F., and keeping Glauber's salt additions down to a minimum, or eliminating the salt altogether. There is no doubt but these help up to a certain point. The most satisfactory results, however, are obtainable by the selection of those dyestuffs which give the best union on rayon and cotton, then dyeing at the boil. By dyeing at the boil better penetration of the seams is assured.

The following dyestuffs have been found to give good results because of their good fastness to acid finishing, and their ability to unionize well on cotton and rayon: Pyrazol Fast Yellow RSW, Pyrazol Fast Orange GH, Pyrazol Fast Brown BRL, Pyrazol Fast Orange 2RN, Visco Copper Blue EG, Chloramine Fast Scarlet 2BSW, Pyrazol Fast Violet R, Pyrazol Fast Violet 4BL and Chloramine Orange B.

Our choice of colors for a general utility formula for the dyeing of various types of rayon-cotton-silk mixtures has been: Pyrazol Fast Yellow RSW, Pyrazol Fast Orange 2RN, Visco Copper Blue EG and Chloramine Fast Scarlet 2BSW, because these colors also leave the silk white in a soap bath. The silk colors used are those normally used in the dyeing of full-fashioned hosiery, and preferably those which do not stain cotton heavily.

SILK AND NYLON

In consideration of the interest being shown in regard to the dyeing of silk hosiery containing nylon, it may be appropriate to make a few general remarks on the subject at this time.

Based on our experience, this preliminary discussion may serve to give some idea as to the behavior of nylon toward various groups of dyestuffs when dyed in conjunction with silk from a soap bath.

The dyestuffs used in these experiments are dyestuffs familiar to the hosiery dyer and for convenience are grouped according to the following classifications:

Group 1—Direct colors.
Group 2—Acid colors which dye from a soap bath.
Group 3—Acetate colors.

Our tests in these experiments were made on tubing consisting of about equal parts of nylon and degummed silk and a small percentage of mercerized cotton, and dyed at the boil for ¾ of an hour, with 6 per cent of soap, ½ per cent color and 4 per cent calcined Glauber's salt.

Results of Tests

Direct Colors: These may be subdivided as follows:

(A) Direct colors which dye the cotton but which do not dye the nylon or the silk, from a soap bath. Examples: Pyrazol Fast Red 7BSW, Chloramine Black BGS, Pyrazol Fast Orange GX and Pyrazol Fast Yellow RSW.

(B) Direct colors which dye the cotton and the silk, and dye the nylon only slightly, from a soap bath. Examples: Pyrazol Fast Brown BRL, Pyrazol Fast Yellow 4GL and Chloramine Red B.

(C) Direct colors which dye the nylon deeply from a soap bath and tend to produce a union on all three fibers. Examples: Chloramine Orange B, Direct Yellow 5G, Chloramine Fast Red F and Viscolan Fast Brown SR.

Direct colors in general show less affinity for the nylon than they do for the silk when dyed on cotton-silk-nylon, from a soap bath.

Acid Colors Which Dye Silk from a Soap Bath: These may be subdivided as follows:

(A) Acid colors which tend to dye union on nylon and silk. Examples: Azo Silk Red 6B, Azo Silk Red 3B,

Xylene Milling Yellow S, Sulfonine Brown 2R and Xylene Milling Navy 4B.

(B) Acid colors which dye the silk much heavier than the nylon. Examples: Sulfonine Red RS, Sulfonine Yellow PR and Sulfonine Orange GS.

(C) Acid colors which dye the silk and leave the nylon practically white. Examples: Xylene Brilliant Cyanine 6B, Xylene Brilliant Cyanine G, Xylene Fast Violet R and Xylene Milling Red R.

Acetate Colors: Acetate colors generally dye the nylon considerably heavier than the silk. Examples: Artisil Direct Yellow GL, Artisil Direct Orange 2R Conc., Artisil Direct Scarlet GP Conc., Artisil Direct Violet BP Conc. and Artisil Direct Blue BSQ Conc.

These dyeing tests were then repeated on the same nylon-silk tubing in a neutral bath, using 2 per cent Sandozol KB, which is a highly sulfonated oil, as the dyeing assistant instead of 6 per cent of soap. All these acid and direct dyestuffs showed a tendency toward shifting their union in the direction of the nylon. Dyestuffs which formerly dyed silk and nylon approximately the same depth when dyed from a soap liquor, dyed the nylon heavier than the silk when dyed from a neutral bath.

The acetate colors when dyed from a neutral bath produced dyeings on nylon and silk practically identical to those produced from a soap bath, and the silk was stained about the same in either case.

There is a wide range of acid colors which although they do not dye silk and nylon from a soap bath will dye either fiber in a neutral bath. In this classification two groupings may be made; those which dye the silk heavier, and those that dye the nylon heavier.

It is our opinion, based on the work thus far completed, that the neutral dyeing of nylon and silk mixtures is not as advantageous a procedure as dyeing from a soap bath.

The tests in these experiments indicate that by choosing the proper dyestuffs it is possible to dye union shades on nylon and silk mixtures from a soap bath.

Dyeing may be started with acid or direct colors, or a combination of both, which tend to dye union, but which leave the nylon lighter than the silk. Acetate colors are added, to shade the nylon, while the silk is still on the light side of the shade to be matched because acetate colors stain silk and this must be taken into consideration. A selected group of acid colors which leave nylon practically white may be used for shading the silk.

If cotton is present this may be shaded with those direct colors which leave nylon and silk white.

We wish to acknowledge the helpful suggestions given by Mr. Louis Zisman, of the Gotham Silk Hosiery Company, in the preparation of this paper.

OLIVE DRAB UNIFORM COLORS

THE American Association of Textile Chemists and Colorists has been asked to co-operate with the United States Government in an investigation aimed at the improvement of woolen and worsted Olive Drab Uniform Fabrics with respect to color fastness.

A committee has been appointed to co-operate with the Quartermaster Depot in determining the most suitable Dyes and Methods of Application to produce fabrics that are satisfactorily fast to Light, Weather and other color destroying agencies.

The personnel of this Committee is as follows:

Chairman—Dr. L. A. Olney, Director of Research for the AATCC.

Secretary—Bertil A. Ryberg, Associate Director of Research for the A.A.T.C.C.

Representing Textile Manufacturers.

Alex. Morrison—American Woolen Co., John N. Dalton—Pacific Mills; Werner von Bergen—Forstmann Woolen Co.; Hugh Christison—Arlington Mills; Roland E. Derby—M. T. Stevens & Sons Co.; Paul N. Otto—Botany Worsted Mills; Robert O. Dietz—Marshall Field & Co. Representative to be named—Peerless Woolen Mills.

Representing Dyestuff Manufacturers.

Daniel P. Knowland—Geigy Co., representing Swiss Dye Interests.

J. Robert Bonnar—General Dyestuff Corporation.

Warren J. Zinck—E. I. duPont de Nemours & Co.

Wm. R. Moorhouse—National Aniline & Chem. Co.

Willard H. Watkins—Calco Chemical Co. Div. of American Cyanamid.

Representing the Quartermaster Depot.

For the Commanding General: H. S. Harpole, Major, Q.M.C., Assistant.

Under the direction of this Committee, extensive tests are being made at the Lowell Textile Institute, which involves testing of not less than two hundred samples.

Make Your Reservations Now for the

ANNUAL MEETING and CONVENTION

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Twenty-first

ANNUAL MEETING AND CONVENTION

HEADQUARTERS

Entrance to the Carolina Hotel, Pinehurst, N. C., where a warm and friendly welcome awaits each new arrival.

General Chairman
SAMUEL L. HAYES

Auspices of
PIEDMONT SECTION

OCTOBER 31ST – NOVEMBER 1ST
THE CAROLINA, PINEHURST, N. C.

TRADE NOTES • NEW PRODUCTS

• JOINS ATLAS COLOR

Samuel A. Stubbs of Lowell, Mass., has joined the selling force of the Atlas Color & Chemical Company, as salesman and demonstrator.

Mr. Stubbs has had practical experience in the dyeing and finishing of all kinds of fabrics and in the past has been connected with some of the largest textile plants in the New England section.

• INDUSTRIAL SPECIALISTS, GOVERNMENT JOBS

The Government continues its search for specialists in all branches of industry and business. The Federal Civil Service examination for Industrial Specialist, announced on July 7, has been amended to remain open for receipt of applications until further notice.

The National Defense Program needs men with experience in one or more of the following fields:

Iron and steel
Non-ferrous metals
Machine tools
Ordnance
Aircraft, marine and automotive equipment
Railroad repair shops
Radio and other electrical equipment, supplies and apparatus
Textiles
Forest products
Paper
Printing and publishing
Chemicals and allied products
Plastics
Petroleum and coal products
Rubber products
Stone, clay and glass products
Leather and its manufactures
Food and kindred products

Salaries range from $2,600 to $5,600 in the various grades. No written examination is given. Application forms may be obtained from Civil Service Representatives at any first- or second-class post office or at a Civil Service District Office.

• SENIOR COTTON TECHNOLOGIST

Charles F. Goldthwait is now senior cotton technologist in charge of the modified finishing section of the cotton chemical finishing division of the new Southern Regional Research Laboratory at New Orleans.

• CIBA REVIEW

Copies of *"Ciba Review,"* number 39, for May, 1941, features the subject of "Madder and Turkey Red." Articles are described by the following titles: The Cultivation of Madder; The History of Turkey Red Dyeing; The Chemistry and Technique of Turkey Red Dyeing; Turkey Red Dyeing in South and Southeast Asia; Notes: Historical Gleanings.

• GENERAL RELEASES

General Dyestuff Corp., 435 Hudson Street, New York City, has released circulars describing the following product:

Acid Cyanine BFA—A bright, acid blue said to possess good fastness to light. It is claimed that, due to its good all-around properties, it is well suited as a base for bright navy blue shades on yarns, ladies' dress goods and hats. Circular G-284.

• SILVER JUBILEE

The Exact Weight Scale Co., Columbus, Ohio, is celebrating their silver jubilee this summer. In 1916 the late Walter S. Smith conceived the idea of pre-determined weighing. Last year he was awarded the Pioneer Award of the National Association of Manufacturers, the only engineer to be so honored in the scale industry. From four or five simple weighing models Exact Weight Scales have expanded to several hundred models for thousands of specialized applications. Where originally three or four industries used this product, fifty-three major industries and several hundred others now use Exact Weight Scales. Exact Weight Scales are standard equipment in all United States arsenals for shell loading purposes.

• NEW PERMOCHART

The Permochart Company, 407 Chestnut Road, Sewickley, Pa., announces production of the new I-EZ (eye-ease) Permochart, a recently improved design of recording instrument chart made for continuous re-use. The new I-EZ Permochart is made in three colors of "Vinylite" plastic, so colored and shaded as to reduce glare and eyestrain to a minimum.

Successfully tested in processes where workmen watched charts for long periods of time, I-EZ charts were said to give definite relief from eyestrain and its resulting fatigue.

The three colors of I-EZ charts, green, ivory and blue, can also be used to advantage in identifying different units or operations, making inspection of charts easier.

Like the white Permochart, colored I-EZ charts are made for all types of recording instruments using circular charts.

• ARIDYE EXPANDS PLANT

The Aridye Corporation, Fair Lawn, N. J., has begun a plant expansion in Rock Hill, S. C. An addition is being built to the present building which will triple the warehouse space now available and double the laboratory facilities.

The expansion is said to be necessitated by the growing use of the Aridye process for printing and padding, and the increased demand for pigment colors to be applied in printing and padding by other methods. Aridye Corporation is now dispersing and selling colors for these types of formulations.

Some manufacturing operations are contemplated in Rock Hill, after the completion of the addition, which should be finished about September 1st.

• APPOINTED SUPERVISOR

William H. Smith, former superintendent of Firth Carpet Company, has been appointed supervisor of the woolen and worsted section of the Textile Unit, research plant of American Viscose Corporation, at Marcus Hook, Pa., it has been announced by Renee Bouvet, manager of the unit. Mr. Smith brings to his new position considerable practical experience in both the woolen and worsted industries, having been connected with Arlington Mills, James Lees and Sons, and M. P. Stevens Company prior to his association with the Firth Carpet Company.

Other Textile Unit appointments include Walter W. Ingenthron, Jr., who has been appointed overseer of worsted combing, drawing, and spinning and woolen spinning; and John T. Drennan, who has been named overseer of preparing, blending, picking, and carding for woolen and worsted yarns. Both men are graduates of the Philadelphia Textile School.

• OFFERS YACHT TO GOVERNMENT

Walter M. Schwartz, President of Proctor & Schwartz, Inc., Philadelphia, builders of industrial drying and textile machinery, offered his yacht to the United States Coast Guard and it has been accepted by Commander I. E. Eskridge of Coast Guard Headquarters. It will probably be used for patrol duty on Delaware Bay. The yacht, "Olif," is 68 feet long and 45 tons.

• SOAP BUYING GUIDE

A new and complete catalog of soaps and detergents, a "Soap Buying Guide," has just been released by the Industrial Department of the Colgate-Palmolive-Peet Company on the 135th Anniversary of the Company's founding.

Covering the entire line of the Company's products from finest toilet soaps to heavy-duty soap products for processing and laundering, it lists the names, packs, qualities and uses of nearly one hundred items. Purchasing agents and buyers for industry can turn to the "Soap Buying Guide" for specific information on soaps and synthetic detergents for power laundering, textile processing, general cleaning of all varieties.

Hotels, hospitals and other institutions will find the "Soap Buying Guide" of defi-

nite value because of the variety of soaps they require. Seventeen toilet soaps are listed in an infinite variety of sizes, colors and scents. Soaps and soap products in flake, powdered and bead form for power laundering are described as well as special detergents for hand dish washing operations. Even dry soap dispensers along with special dry and liquid soaps are included in the "Soap Buying Guide."

The "Soap Buying Guide" is available to all industrial users of soaps and soap products, without charge. It may be had by writing to the Industrial Department of the Colgate-Palmolive-Peet Company, Jersey City, New Jersey.

• NEW BOOK ON TRITON 720

A synthetic detergent called Triton 720 and described as "an aqueous paste of a sulfonated ether salt" is announced by Rohm & Haas Company, Philadelphia, Pa.

Triton 720 is said to produce results not obtainable with other detergents, and a typical case is cited in which a combination of 1% Triton 720 and ½% ammonium bifluoride removed greasy iron spots from a white rayon fabric that could not be cleaned in any other way. In concentrations ranging from 1/10% to 1%, Triton 720 is reported to give superior results in the more usual textile scouring applications.

Among the other properties of Triton 720 which are claimed in a new book released recently are the following: It eliminates scouring or kier boiling of certain rayon and cotton fabrics, may be applied in the desizing bath or it may be padded on separately, thus eliminating the intermediate scouring process. Also, the addition of Triton 720 to printing pastes assists penetration and produces sharper prints. Used with soap in the final bowl in wool scouring, the new product is said to improve greatly the appearance and physical characteristics of the wool, making it whiter and loftier and more easily rinsed.

Copies of the book may be obtained from Rohm & Haas Company, Washington Square, Philadelphia, Pa.

• WASHABILITY, SPUN RAYON HANDKERCHIEFS

Results of an exhaustive laundering research on Crown Tested spun rayon handkerchiefs have been announced by American Viscose Corporation. The investigation, which was conducted by Better Fabrics Testing Bureau, included two series of tests, one on hand-washing and one on bleach laundering. Wet strength, dry strength, shrinkage, and weight were accurately determined at intervals throughout the progress of both tests. The handkerchiefs tested were of both men's and women's types produced by Hermann Handkerchief Company.

The hand-washing tests were extended over 79 launderings, each of which consisted of a three-minute period of sudsing, followed by a scrubbing action in a neutral soap solution at 100°F., rinsing in three waters, and rotary ironing. According to the laboratory's report, the handkerchiefs withstood the 79 washings before showing visible damage. This, it is pointed out, is equivalent to three years of normal wear at the rate of one washing every two weeks. At the same time, shrinkage and loss of strength had not exceeded the useful limits, while weight loss was negligible. The report summarized the hand-washing tests with the statement: "no special precautions are necessary in the washing of these spun rayon handkerchiefs other than to avoid the use of a bleach. These fabrics may be boiled in hot water and soap without harmful effects."

Bleach-laundering tests were run through 40 launderings for the men's handkerchiefs. and 41 for the women's handkerchiefs. Each of these launderings consisted of a 40-minute run in suds at 160° F., during the last 10 minutes of which a hypochlorite bleach was added. Handkerchiefs were then rinsed in three waters and rotary ironed.

At the completion of the tests, which are said to be equivalent to considerably more than one year's service, the handkerchiefs showed slight signs of wear both in hems and in the body of the fabric. This deteriorating effect of the bleach solution was expected, it is stated, and for this reason the tests were conducted under the same conditions employed by laundries in the washing of linen and cotton handkerchiefs. Since the measured loss of strength, loss of weight, and shrinkage remained within the limits of practical service, the ability of the handkerchiefs to withstand at least a year of normal service is said to be established by the tests, regardless of whether the fabric is hand-washed or laundry-washed.

• TECHNICAL NOTES FROM FOREIGN SOURCES •

"Textilosophy"

R. Haller—J. Soc. Dyers & Col., 56-425, *Oct.*, 1940.—The sense of relationship between Nature and technology has been almost lost to us; rather we are impressed by the *effects* produced by technology, and we pride ourselves on how far we have progressed in this respect. It may not be deemed superfluous if textile technicians are reminded of the functions which the natural textile fibers and natural dyes originally had; the purposes served by these organisms were far removed from those to which man has put them.

The most prominent elements of the textile industry are the fibers and the dyes. Considering only the natural fibers, it will repay us if we first of all give a little thought to the biological object of these creations. Cotton, flax and wool were not created, as some appear to believe, with the sole object of permitting mankind to prepare yarns and cloth therefrom.

The cotton fiber appears at first sight to play the biological role of an apparatus for use in flying, having as its object the dissemination of the seeds by the wind. Against this theory, however, a large number of arguments may be quoted. First, the cotton seed is far too big in comparison with the fiber length of the seed hair, and it is far too heavy to be able to travel long distances through the atmosphere by mere force of wind currents. If it is compared with other seeds, such as those of the willow or the poplar, which actually possess flying apparatus, it will be seen that in these cases the length of the hairs is at least 50 to 100 times greater than the seed, while the relationship of hair to seed in the case of cotton even in the most favorable circumstances is no greater than 6 to 1.

Further contradictions against the functioning of the seed hairs of the cotton plant as flying apparatus are offered by a microscopic comparison of these fibers with the seed hairs of the willow, the poplar, the reed mace and others, all of whose hairs are actually used as flying apparatus. While the cotton fiber possesses a lumen which is comparatively narrow, i.e., it has a greatly reduced inner air space and disproportionately well-developed cell walls, the other plants have very well developed voluminous inner spaces and very thin walls, i.e., on account of their disproportionately low specific gravities they have ideal proportions for a seed which is to be spread by the wind. Apart from the morphological differences, microscopic

examination discloses further primary divergences, such as the exceedingly fine cuticle of the cotton fiber cell wall and the spiral structure of the lamellae which compose it. It is also to be emphasized that all wild varieties of cotton possess a very much shorter staple than that obtained from the cultivated species, which have been produced by careful selection of appropriate strains, and this again speaks against the acceptance of the flying apparatus theory.

This hair must, therefore, have quite another function than that universally ascribed to it. The suggestion has been made that the cotton hairs absorb moisture and so assist germination of the wild-growing plants, though this explanation of their biological importance contains much that is problematical. In the author's opinion, the seed hairs are organs which are used by the seed in accommodating itself to the varying climatic conditions, and are designed to protect the seed from too great loss of moisture, which would probably carry in its train certain germination difficulties. In spite of all attempts to solve this problem, none of the solutions hitherto put forward has proved entirely satisfactory, and it remains a biological enigma.

In the matter of their biological significance, the bast fibers play a much less equivocal role. They are consolidating elements against strains put upon plants which have developed extraordinarily in an upright direction—the hemp fibers alone need to be mentioned—against pulling, on the one hand, and against cracking and bending on the other. Here the practical purpose governing natural phenomena is obvious, and this is also demonstrated by the construction of the fiber, which, by its systematic contiguity of structural elements, is admirably suited to this purpose. The same type of structure is exhibited by the flax and ramie plants, as well as by others, such as the nettle and broom, which have served for the production of fibers.

If we now consider the artificial fibers, such as the rayons to-day manufactured in such enormous quantities, it must be admitted that their inventors not only worked in a marvelous technical manner, but also created a new economic impetus. Concerning the fine structure of the rayon fibers, however, we have to admit that it remains far behind the natural fibers in its suitability as a fiber structure. We see Nature as the mistress of the creation of fibers, and man's ability has only succeeded in producing products which, if we are to judge objectively, show certain similarities to the natural fibers in their appearance, but which are not comparable in either their physical properties or their chemical behavior, i.e., they are obvious substitutes. It must also be remembered that in the manufacture of these artificial fibers the vegetable raw material cellulose is used as parent substance, a material created by the plant itself by methods which, in their chemistry, still remain almost a mystery to us. It may be noted in passing that the new American creations in this field, which are claimed to be fibers possessing a tensile strength hitherto unknown, are, however, definite artificial materials, which scarcely permit comparison with rayon obtained by the regeneration of cellulose.

Taking wool as the first member of the class of animal fibers, we find that both in its structure and in its chemical composition it is completely non-homogeneous. Different chemical individualities, each with a different dyeing behavior, are bound together into one highly complicated body. In the outer layer the cells form a system in which the individual cells are held together by means of a cementing substance, Lanain. The separate cells are completely independent entities, each possessing a relatively wide lumen, which is able to enclose a certain quantity of air. Such a complicated structure, which is particularly to be observed from a cross-section of the fibers, is naturally incapable of reconstruction by artificial means. This is evident by examination of cross-sections of an artificial wool, "Lanital." We observe here nothing more or less than a compact rod, which only differs very slightly from certain types of rayon. It would be perfectly plain from consideration of this cross-section that such a creation could never be seriously competitive with the wool fiber from a mechanical viewpoint. Here, also, the work of Nature has not even been approximated.

The conditions which we find in regard to natural silk are entirely different. It might even be said that we are dealing here with a pseudo-industrial product. In principle, the spinning process that the silk worm carries out is almost identical with the technicalities of the rayon manufacturing process. Nevertheless, the former is ap-

Expert Witness

In the "Scientific and Industrial Notes" section, Journal of the Society of Dyers and Colourists, September, 1940, is printed an example of the ability displayed by an expert witness in a case involving chemistry to make clear in court the meaning of certain rather obscure scientific terms. As the incident related apparently took place in connection with United States patent law, it may stand repeating for the benefit of those who have not seen the original.

Orientation in connection with the relativity of two substituents in the benzene ring was explained by the witness as follows:—"Your Honor, the question of substituents can be compared with the turtle. As your Honor knows, the ordinary turtle has his head opposite to his tail and is therefore a para-turtle. If he were deformed by having his tail in the place of a foreleg, he is an ortho-turtle, while if his tail replaced a hind leg he would be a meta-turtle. As reptiles they would not be alike." The court saw the point. In another case, an expert defined enantiomorphous isomers as left-handed and right-handed identical twins.

preciably more complicated; the thread which leaves the spinning gland consists of two separate threads, united by an adhesive, sericin. Structurally, the natural fiber differs from the artificial by the presence of a fine fibrillary structure and by the presence of fine canals which penetrates the fibroin, a feature of the silk fiber which has only recently been discovered and which is called upon, undoubtedly, to play an important part in the process of silk weighting. We thus see in the fiber a product which in certain respects may be placed beside the rayons, yet which differs from them on account of its exceptional fineness of structure and appreciably more favorable properties.

Different conditions are to be found among dyes, which, next to the fiber themselves, are the most important part of textiles. Modern coloring matters are so completely built upon the basis of synthetic work that it appears as if mankind has scarcely left anything more to be done in this field. It may, nevertheless, be profitable to draw some comparison between the work of the plant world and that of the technical manufacture of our dyestuffs in use. We cannot deny that even to-day it is plants which provide us with the raw materials necessary for the synthesis of our dyes. Plant life thousands of years ago died and fell into decay, and in the course of time has undergone powerful, spontaneous chemical changes, culminating in the coal from which we obtain the necessary parent materials for our synthetic work.

If we look at the work of the vegetable kingdom we are confounded by the apparently simple agents by which the most elaborate synthesis are carried out. Such artificial dyes as Indigo and Alizarine only see the light of day after a series of interlocking chemical reactions, which include high pressures and elevated temperatures. These agents are not available to the plants for the production of the same dyes, and the ways they adopt in forming these products must be essentially different from those devised by human intelligence. If we probe deep into the working of the plant and observe the highly complex chemical operations which it performs we realize that we are standing before a phenomenon the like of which is nowhere to be found in the whole chemical technology directed by mankind.

We have as yet scarcely any idea of the way in which the plant manages to produce, for example, cellulose and the various types of sugar. Our chemical industry, and in particular our textile industry, is built upon the utilization of cellulose. In its use we are drawing upon our stores of one of the most important raw materials, one which is supplied to us only by the vegetable world. Why should we not learn from the plant how to build up cellulose for ourselves out of its elements, carbon, oxygen and hydrogen? In this way we should avoid the reproach that we have squandered in our irresponsible manner the patrimony of Nature.

This unusual paper, which closes with a quotation from Paracelsus and whose arresting vein of philosophical speculation is done scant justice by condensation, is from the Ciba Laboratory at Basle. The distinguished author justifies its "somewhat surprising" title in light of the Aristotelian definition of philosophy as the examination of the origin and principles of all things, in this case applied to questions arising in the study of textile technical problems.

Comparative Observations on the Swelling of Jute Fiber

Macmillian and Sen—Jour. Text. Inst., XXXII, 3, *T*45, *March,* 1941.—In a previous paper it had been shown that measurements of "diameter" by means of the microscope are unsuitable for the accurate determination of swelling in jute fibers. The present investigation deals principally with specific gravity determinations, their utilization in calculations relating to swelling and measurements on cross-sections of jute fiber for the determination of swelling.

Apart from its use for the determination of swelling, the specific gravity of jute fiber is, in itself, an important physical constant entering numerous calculations on fiber and yarn diameters, wetting, etc. The specific gravity of a solid which neither absorbs nor is soluble in water is equal to the weight of the substance in air divided by the weight of its own volume of water. Textile fibers, however, absorb water and swell. Since the volume of water absorbed is greater than the increase in volume of the fiber on swelling, a contraction in total volume must take place so that the resulting apparent specific gravity is appreciably greater than the true one. This difference will depend upon the magnitudes of the absorption and the swelling. If, however, the fibers are saturated with water, and therefore completely swollen before immersion, it is possible to obtain a true specific gravity using water as the medium. In all cases of incomplete saturation between absolute dryness and 100 per cent relative humidity, true specific gravities may be determined with the specific gravity bottle by immersion of the fibers in a non-swelling liquid.

In the experimental procedure followed, the dry weight of the prepared fiber was determined both by a desiccator and by a regain bottle method. Specific gravity was then determined by means of the specific gravity bottle, using as different liquids for the determination water, benzene, carbon tetrachloride, acetone and mineral oil. Observations of fiber swelling and diameter swelling measurements were made microscopically. Results are expressed in a series of tables and one graph.

It was found that the true and apparent specific gravities or dry jute fibers are 1.436 and 1.559 respectively. The volume swelling of fibers calculated from the specific gravity is 45 per cent. Measurements on cross-sections as well as on diameters indicate that swelling diminishes with increase of area or diameter of fibers.

THE ROLE OF CYSTINE

(Continued from page 430)

iodide ethylene dibromide, trimethylene dibromide, and tetramethylene dibromide show such a trend (Table 3).

TABLE 3

Thirty per cent indices and breaking strengths of wools reduced and alkylated with alkyl dihalides.

Treatment	*30 Per Cent Index*	*Breaking Strength*
		Grams
Untreated	0.99	1310
Reduction and CH_2I_2	0.94	1380
Reduction and $(CH_2)_2Br_2$	0.92	1420
Reduction and $(CH_2)_3Br_2$	0.90	1460
Reduction and $(CH_2)_4Br_2$	0.88	1380

The breaking strengths of yarn treated like the fibers show similar trends (Tables 1 and 3). Reduced wool, reduced and methylated wool, and wool reduced and treated with chloroacetic acid were markedly lower in breaking strength than the untreated wool, while wool that had been reduced and alkylated with monohalides of high molecular weight, or with a dihalide, was not far different from untreated wool in this respect.

(*b*) *Hygroscopicity*

The hygroscopicity of the modified wools varied depending on the chemical nature of the groups introduced into the wool, as shown in Tables 4 and 5. Wools into which large groups have been introduced by alkylation with benzyl chloride, *p*-chlorobenzyl chloride, heptyl bromide, or dodecyl bromide were found to be less hygroscopic than untreated wool. By introducing hydrophobic groups of high molecular weight into the wool the percentage of hydrophilic structures such as peptide bonds, is decreased, and as a result the products are less highly hydrated.

TABLE 4

Alkali-solubility and hygroscopicity of wools reduced and alkylated with monohalides.

Treatment	*Alkali-Solubility*	*Moisture Content*
	Per Cent	*Per Cent*
Untreated	10.5	16.0
Reduction	ca. 50.0	...
Reduction and reoxidation	12.5	16.3
Reduction and CH_3I	33.0	16.3
Reduction and C_2H_5Br	18.3	16.2
Reduction and $C_6H_5CH_2Cl$	15.4	14.8
Reduction and p-$ClC_6H_4CH_2Cl$	12.8	14.0
Reduction and $C_7H_{15}Br$	18.0	15.6
Reduction and $C_{12}H_{25}Br$	18.2	15.6
Reduction and $ClCH_2COOH$	ca. 50.0	16.9

TABLE 5

Alkali-solubility and hygroscopicity of wools reduced and alkylated with dihalides.

Treatment	*Alkali-Solubility*	*Moisture Content*
	Per Cent	*Per Cent*
Untreated	10.5	16.0
Reduction and CH_2I_2	5.2	16.4
Reduction and $(CH_2)_2Br_2$	6.6	16.2
Reduction and $(CH_2)_3Br_2$	5.3	16.0
Reduction and $(CH_2)_4Br_2$	7.0	16.3

The introduction of small groups by alkylation with methyl iodide, ethyl bromide, or an alkyl dihalide of low molecular weight should lead to introduction of only a small percentage of hydrophobic groups. As would be expected, these products were found to be very little different from untreated wool in hygroscopicity. The introduction of a polar group, as by reduction and alkylation with chloroacetic acid, yielded products that were somewhat more hygroscopic than untreated wool.

(*c*) *Alkali Solubility*

Reduction of wool, followed by alkylation with an alkyl monohalide may be expected to render the wool more readily soluble in alkali, since this process breaks disulfide bonds which form links between polypeptide chains, and therefore decreases the average molecular weight of the wool proteins. The high alkali-solubilities of wool that has been reduced and treated with alkyl monohalides illustrates such a behavior. The extremely high alkali-solubility of wool alkylated with methyl iodide may be due to the formation of sulfonium groupings according to the following equation:

$$WSCH_3 + CH_3I \rightarrow W\,S(CH_3)_2^+ + I^-$$

Methyl iodide is known to be exceptionally reactive in this respect[22]. Sulfonium compounds are highly ionized and would be expected to increase the alkali-solubility.

Reduction breaks disulfide cross-linkages, a process which lowers the molecular weight and at the same time introduces ionizable sulfhydryl groups into the wool. Each of these changes should tend to increase the solubility of the wool in alkali, and observations confirmed this expectation. In view of these results, it is apparent why strongly alkaline solutions of thioglycolic acid, as observed by Goddard and Michaelis[7, 8], are capable of dissolving wool. Reduction followed by alkylation with chloroacetic acid should also yield products that possess high alkali-solubility, since carboxyl groups also are ionized in alkaline solution. Such wool was found to be very readily dissolved by alkali.

Reduction of wool, followed by treatment with polymethylene dihalides such as methylene iodide, ethylene dibromide, trimethylene dibromide or tetramethylene dibromide, maintains the original molecular weight of the protein, and also replaced disulfide cross-linkages, which

are unstable toward alkali[22], with stable *bis*-thioether* cross-linkages as eq. 3 indicates. Such a process was found greatly to increase the resistance of wool to the action of alkali. The alkali-solubilities (Table 5) of these samples were much lower than those of untreated wool, or of any of the wools reduced and then alkylated with alkyl monohalides.

(*d*) *Effect of Varying the Extent of Reduction and Alkylation*

The results described in the preceding sections were obtained from wool that had been reduced to nearly the same cystine content and then alkylated. The relation between the extent of reduction and alkylation, as judged from the decrease in content of unchanged cystine and the properties of the products, has also been studied, using two of the alkylating agents· methyl iodide and trimethylene dibromide. The experimental results are summarized in Table 6.

TABLE 6
Properties of wool reduced to indicated cystine content and alkylated with indicated reagents.

Cystine	*30 Per Cent Index*	*Breaking Strength*	*Alkali-Solubility*
Per Cent		*Grams*	*Per Cent*
A. Untreated			
12.2	0.99	1310	10.5
B. Alkylated with $(CH_2)_3Br_2$			
10.3	0.99	1338	5.8
6.0	0.86	1318	3.7
4.0	0.72	1272	2.6
2.2	0.68	1012	2.5
C. Alkylated with CH_3I			
10.3	0.73	1287	13.2
6.0	0.48	1250	31.5
4.0	0.27	1240	43.5
2.2	0.18	989	83.0

It is apparent that in both cases the 30 per cent index decreased as the extent of reduction and alkylation increased. Fibers that had been reduced and methylated however, were decidedly more changed in this respect than those which had been reduced and treated with trimethylene dibromide. The breaking strengths of yarn treated along with the fibers show the same trend as the 30 per cent indices, but are considerably less sensitive measure of the changes that have taken place.

Of particular interest is the fact that, while the alkali-solubility of the reduced and methylated wool increased as its content of unchanged cystine decreased, that of the wool reduced and treated with trimethylene dibromide decreased. This contrasting behavior furnishes further evidence that reduction followed by methylation breaks disulfide cross-linkages and decreases the average molecular weight of the wool protein, while reduction followed by treatment with trimethylene dibromide maintains the molecular weight by rebuilding cross-linkages of a type that are extremely stable to alkali.

*This terminology is in accord with the suggestions of Patterson and Curran[23].

Susceptibility to degradation by alkali, which has been one of the most important practical disadvantages of wool, can now be overcome to a large extent through conversion of relatively unstable disulfide cross-linkages to extremely stable thioether cross-linkages. The stability of wools of this sort, under a variety of conditions of practical interest, is now being investigated in this laboratory.

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